Optimization of a Fluidized Bed Isothermal Reactor in a Styrene Production Process

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Abstract

The focus of this thesis is to explain the optimization of a fluidized bed isothermal reactor in a styrene production process. The first section of the thesis gives a summary of chemical process optimization in general. The next portion of the thesis gives an introduction to chemical process simulation software, and it explains how simulation software aids in the design and optimization of chemical processes. The third section of the thesis gives a brief overview of an optimization project of a styrene production process that was completed in the previous semester with a group of three. The final section explains the optimization of a fluidized bed reactor in the styrene production process discussed in the previous section of the thesis. The results of the reactor optimization produced a reactor system that has a total fluidized catalyst bed volume of 75.4 m^3 with 15 reactors in parallel. The optimized reactor operates at a temperature of 715°C and a pressure of 75 kPa, and it produces a total flowrate of styrene of 193 kmol/hr and yield of ethylbenzene to styrene of 68 %.

Contents:

Introduction to Engineering Process Optimization and Design

This section overviews key engineering process design and optimization concepts and purpose. The ultimate goaal of process design and optimization is to improve the process. Richard Turton's book named *Analysis, Synthesis, and Design of Chemical Processes* defines optimization as "the process of improving an existing situation, device, or system such as a chemical process[1]." The activity of optimization involves using creative approaches to examine multiple options for process changes that focus on optimizing a chosen objective function. The objective function of a process is a mathematical function that the person optimizing attempts to minimize or maximize by finding the best values for the decision variables. The decision variables, or design variables, for a process are those variables that the engineer has a degree of control over. These variables may be of two different types, continuous or discrete. Continuous variables are such things as temperature and pressure, while discrete variables are integer values such as the number of stages in an absorption column. All decision variables have certain value limitations called constraints. A constraint for an optimization can involve multiple decision variables. Therefore, the true goal of optimization is to minimize or maximize one or more objective functions while remaining within the constraints of the decision variables. For all optimization problems a global optimum exists. The optimum is the point where the objective function reaches the best possible value with all decision variables within their constraints. The global optimum is the best possible solution to an optimization problem. This value will never be found in any

optimization or design problem, but the objective is to get as close as possible to the global optimum value.

All optimizations begin with an initial base case. Therefore, a defined process must exist that the optimization process can improve upon. The base case process design may be an actual operating plant or just a conceptual process flowsheet, but it must be a defined process. To start the optimization of a process, selecting the best base case design available for the starting point is ideal. Analysis of the base case design must be able to give a calculation of the objective function of the optimization. Therefore, the base case design needs to contain at least enough detail to produce the calculations necessary for finding the objective function of the optimization. It is also imperative that the analysis of the base case also includes enough detail to show the result of changing key decision variables on the objective function. Finding the values of key decision variables that maximize or minimize the objective function is the goal of a process optimization. Therefore, a calculation of the effect of the decision variables on the objective function must be possible in the base case.

An important step in beginning the optimization of a process is to choose the scope of the base case to optimize. The scope may be a single piece of equipment, multiple pieces of equipment, or an entire plant. After choosing the scope of the optimization of the base case, the next step in the optimization process is to choose the objective function. As stated earlier, selection of the objective function must have an extreme maximum or minimum value as its goal. Choosing the objective function wisely is very important to the success of the optimization. If

a vague or badly chosen objective function is the goal of an optimization, then the results of the optimization will not be useful. In most process optimizations, the objective function chosen is one with units of dollars. Commonly used objective functions are the net present value of a process (NPV) or the equivalent annual operating cost (EAOC). Depending on the scope of the process chosen to optimize, the objective function may not always be directly centered on economics. Therefore, a smaller scope may have as its objective function the maximum yield of a reactor or the minimization of the concentration of some contaminant from a waste stream. The most important part of choosing the objective function is to confirm that a rational basis for its selection as the objective function exists whether it is monetary or nonmonetary.

After choosing the scope and defining the objective function of the optimization process, an evaluation of the base case process needs to take place in order to decide the targets of an optimized process. The initial analysis of the base case produces a goal for the optimization, and it also charts out a path by which to move towards the solution. This analysis usually leads to the identification of the most important decision variables. The key decision variables are the ones that affect the objective function in the largest way. Some decision variables affect the process and the objective function more than others. Therefore, various decision variables prove to be more important or less important based on the base case analysis. Identification and prioritization of the decision variables is the last step before truly beginning to optimize the process. The optimization process takes

place by varying the decision variable to find the values that give the optimum objective function.

The methods of finding these optimum decision variables are topological and parametric optimization. Typically, topological optimization is the first method of optimization employed. Topological considerations usually come first in optimization, because it is much easier to optimize parametrically after the designation of the flowsheet topology. Some processes require the use of topological and parametric optimization procedures simultaneously, but consideration of any large changes in process topology usually comes first in the optimization process. The main focuses of topological optimization include finding the optimum method for the following issues: elimination of unwanted by-products, rearrangement or elimination of equipment, alternative separation methods or reactor configurations, and improved heat integration. Addressing these questions according to the order in which they are listed is beneficial in finding the optimized topology for a process. After setting the topology of the process flowsheet, the next step of the optimization is to use the method of parametric optimization to find the optimum parameters for the process. Examples of some important issues to address in parametric optimization are the following: reactor operating conditions, single-pass conversion in the reactor, recovery of the unreacted materials, reflux ratios, operating pressure of separators, and purity of products. Much of the time the tool used for both types of optimization is simulation software that can vary multiple decision variables at the same time within their constraints in order to maximize or minimize a given objective function

Introduction to Chemical Process Simulation Software

Chemical process simulation software is a very useful and effective tool to aid in the optimization of a chemical process. Simulators can carry out both topological and parametric optimizations. A process simulator is very powerful tool that engineers use to aid in optimization, design, and troubleshooting of chemical processes. All process simulators have six main components. These elements are the following: component database, thermodynamic model solver, flowsheet builder, unit operation block solver, data output generator, and a flowsheet solver. The engineer using the simulator must be very familiar with the software system and able to use all these elements effectively in order to setup a process accurately. Each part of the simulator has a different function. The component database stores all the constants needed to calculate physical properties from the thermodynamic models. The thermodynamic model solver uses a chosen thermodynamic system to calculate and estimate properties. The flowsheet builder displays graphically the flow of the streams and equipment. The unit operation block solver performs numerous calculations on various pieces of equipment in the process. Output reports and data generation come from the data output generator. This element of a simulator can customize simulation results and consolidate them in a report or graphical form. The flowsheet solver governs the sequence of the flowsheet calculations, and it controls the overall convergence of a process simulation.

In order to setup a process simulation a user needs to follow a few general steps. The first step in setting up a process is the selection of all the chemical components present in the process from the component database. After selecting

the correct chemicals from the database, the next step is to select a thermodynamic package to make the calculations in the simulator. Selection of the thermodynamic model is a very important part of the simulation setup, because choosing an incorrect model for the simulator produces inaccurate results that are not useful to the user. Sometimes the thermodynamic model is different for each piece of equipment. Some options for these models include packages that calculate for one liquid phase or two liquid phases. The user must be sure to know the phases and conditions in each piece of equipment in order to accurately setup the thermodynamic model. Having selected the correct thermodynamic model for each piece of equipment, the next step is to input the particular flowsheet topology. Creation of the flowsheet topology involves designating and specifying the input and output streams for each piece of process equipment in the simulation. Definition of the feed stream properties comes next in the setup. The user must specify all of the properties of the streams feeding into the process including the temperature, pressure, flowrate, vapor fraction, and composition of the streams in order to accurately simulate the process. After specifying the feed stream properties, the parameters of the process equipment need specification. These parameters will be some of the variables that change in order to optimize for the objective function. The final step in the simulation setup is the selection of how to display the results and the method of convergence. After selecting the convergence method and the desired display of the results, the user can run the simulation and obtain a solution.

In order to optimize a process using a simulator, the base case process must be setup correctly in the simulator according to the steps discussed in the last

paragraph. After setting up the base case process in the simulator, the user can use the methods of topological and parametric optimization to improve the process. To optimize a process in a simulator, an objective function needs to be selected for the process or the piece of equipment to be optimized. Making sure that the process operates inside of its constraints is a crucial part of optimization with a simulator. If the engineer using the simulator is not careful, convergence on the objective function can occur at conditions outside the process constraints. If the process does not remain inside the constraints, then any solution converged upon is useless. The decision variables for the optimization may be topological or parametric in nature. Most process simulators have some sort of optimizer element, or the capability to run case studies on a process. Optimizers and case studies are both useful methods of optimizing with a process simulator. Many times the user employs both tools to optimize a process. The case study feature of a simulator with take an input of a certain parameter, and it will graphically display the effects of varying the parameter over a specified range of values using a designated step size on a chosen objective function. This tool is very useful in optimization, because the user can obtain a graphical representation of how certain parameters affect the process and the objective function. From this information the choice of the best parameters to maximize or minimize the objective function is much more obvious.

An optimizer is also a valuable tool to use in optimization. The optimizer element of a process simulator makes calculating the best parameters to achieve an objective function extremely efficient. The first step in using an optimizer is to designate an objective function and choose to maximize or minimize it. After this

the user selects the constraints for the optimizer to operate under. The final step in setting up the optimizer is selecting the key decision variables. The decision variables need a specification for the range and step size of values in which to optimize. The optimizer has the capability to calculate the objective function using as many decision variables as the user wishes to input. After setting up the optimizer correctly, the user can run the optimizer, and it will converge on the objective function by changing the chosen parameters within the specified ranges under the constraints given. At the click of a button the simulation software allows an engineer to find the best possible values for the decision variables needed to reach a desired objective function. If the optimizer does not find a solution the first time that it is run, then one or more ranges of values for parameters may need changing or expansion in order for the optimizer to converge on a solution. Sometimes the optimizer does not a find a solution, because no solution exists for the parameters given with the equipment specifications defined by the user. The optimizer may require redefinition of the equipment or process specifications in order to find a solution. Running case studies on a process or specific piece of equipment before setting up the optimizer is usually beneficial. The graphical results from the case study give a good idea of how changes in certain parameters affect an objective function. With this knowledge the user can initially set up the ranges of values for variables in the optimizer more accurately. Optimizer and case study functions are very beneficial features of process simulators that allow engineers to improve processes more efficiently.

Summary of the Optimization of Unit 500 Styrene Production Process

As a member of a three-person team last semester, I took part in the optimization of a styrene production plant . Appendix A to this thesis contains the complete details of the optimization. The following is a brief summary of the optimization project in order to help clarify the purpose of the fluidized bed isothermal reactor optimization that is the main subject of this thesis. The goal of the styrene plant is to convert ethylbenzene, via a catalytic reaction, to styrene . Styrene is a monomer that polymerizes to create polystyrene better known as Styrofoam. The production requirement for the process is 100,000 tonnes/yr of styrene of 99.5 wt% purity. Our objective as a team was to optimize the process in order to maximize the net present value, or NPV, while satisfying a set of given constraints.

The first step in the optimization process was to do a preliminary analysis of the base case in order to identify potential revenue and calculate the economic potential of the plant, The economic potential is the potential maximum profit possible for the process. This calculation assumes that all products separate perfectly and that all products can be sold at the pure product prices. Calculations of economic potential showed that it was possible for the process to be profitable. Since the process had the potential to be profitable, we began a more detailed analysis of the base case process. The first step in improving the process is to determine the current base case value for the objective function as a standard for to improve upon. Therefore, the first part of our project involved setting up the base case plant in a process simulator and calculating the net present value of the current

process. After calculating the base case net present value, we began conducting a sensitivity analysis of the base case process in order to find out which variables affect the objective function the most. A sensitivity analysis helps to pinpoint which areas of the process are most important to the maximization or minimization of a desired objective function. The sensitivity analysis indicated that changes in raw materials, revenue, utilities, and the fixed capital investment have the largest impact on the net present value of the process.. Since these factors proved to be key variables in maximizing the net present value, we decided to optimize by addressing these issues first.

The next step in the optimization process began by designing a new reactor section. The reactor section plays the biggest role in maximizing the NPV, because it converts raw material to product. Therefore, since our sensitivity analysis showed that raw materials and revenue had the greatest effect on the NPV, it was obvious that we should focus on the reactors first. Most of the time optimization of the reactor section comes first in a chemical process optimization. It makes sense to optimize the reactor section at the beginning of the optimization process, because the reactor inlet and exit stream specifications determine the requirements for the feed section and separation section of the plant. Optimization of the reactor involved analyzing various temperature, pressure, molar composition and volume conditions within the given constraints of the project. Appendix A presents the constraints in detail. Originally the base case operated with two adiabatic plug flow reactors in series. We optimized the reactor section with the yield of ethylbenzene to styrene as our objective function. Since styrene is by far the most profitable

product of the reactions, and ethylbenzene is a very expensive raw material; yield seemed to be the most appropriate objective function. Yield involves maximizing the conversion of the raw material to desired product.. We improved the reactor performance by redefining some of the inlet parameters and using five parallel adiabatic reactors instead of the original design. The main subject of this thesis is a further optimization of the reactor section of this plant. I will explain the details of this reactor optimization later in the thesis. At this point, I want to continue to summarize the optimization of the entire plant.

After optimizing the reactor section of the plant, we decided to optimize the feed section to the plant in order to fit the reactor inlet requirements. The sensitivity analysis exhibited that utility cost was very impactful on the objective function of maximizing the NPV of the process. In order to address this issue, we found ways to integrate heat in the feed section to achieve the required reactor inlet conditions. Feed section optimization involved a few topological changes. We rearranged the order in which the process stream flowed through various pieces of equipment. Heat integration in the feed section decreased the utility cost of the plant, and it increased the NPV of the process.

The next portion of the plant that we focused on was the separation section. The separation section in a process is extremely important. Improvement of the separation section allows more of the product that is made in the reactor to be sold to increase revenue for the plant. The separation section is also crucial in separating out unreacted raw materials so that they can be recycled and reused in the reactor. If the separation section is not efficient, then raw material and product

will go to waste. In order to maximize the NPV of the process, optimization of the separation section of a plant is vital. We optimized the separation section by changing some of the specifications of the stream leading into the liquid/liquid/vapor separator. This process vessel is the first piece of equipment that separates waste from product in the process. Increasing the efficiency of this vessel helped save styrene product and unused ethylbenzene from being wasted. We also redefined some parameters of the both distillation columns in order to obtain better separation. The changes made to the distillation columns increased the revenue by producing a sellable distillate stream from the first distillation column and by separating ethylbenzene from styrene more efficiently in the second column. Parametric and topological changes to the separation section increased the NPV of the process. Appendix A gives more details on the changes made to the separation section of Unit 500 and the resulting increase of the NPV.

The final step in our optimization process was to address the fixed capital investment cost of the process. The sensitivity analysis showed that the changes in the fixed capital investment affected the NPV of the process greatly. In order to make sure that we maximized the NPV, we researched ways to decrease the fixed capital investment for the plant in order to maximize the objective function. Fixed capital investment for a plant includes the cost of the physical process equipment, and certain construction materials for equipment are much more expensive than others. We made a few changes to materials of construction of a few of the pieces of equipment in the plant that decreased the fixed capital investment for the plant. The biggest change in fixed capital investment came from changing the material of

construction for both of the distillation columns from titanium to carbon steel. Titanium is much more expensive than carbon steel, and certain temperature, pressure, and chemicals require its use. After researching the properties of the chemicals present in the process and analyzing the temperature and pressure operating conditions in the plant, we decided that carbon steel was an appropriate material for most of the process equipment. These construction material changes decreased the fixed capital investment for the process and increased the NPV for the process. These changes concluded our optimization process. Overall, our process optimization increased the NPV drastically, but we recommended further optimization to the process before moving forward with the new plant design.

Fluidized Bed Isothermal Reactor Optimization

My individual project for this thesis was to optimize a fluidized bed isothermal reactor for the production of styrene. An isothermal reactor maintains the same inlet and exit stream temperature, and a fluidized bed is a configuration where the catalyst particles are fully suspended in a fluid. When a bed reaches fluidization the pressure drop across the reactor remains constant with increasing superficial velocity, but the bed height continues to increase with increasing fluid flow. Minimum fluidization velocity is the superficial velocity of the fluid in a fluidized bed at which the drag force by the upward moving fluid is equal to the weight of the solid particles. A crucial operating constraint given in the project statement for this fluidized bed reactor is that the superficial gas velocity in the reactor remains within the range of 3 to 10 times the minimum fluidizing velocity. Figure 1 below displays the effect of superficial velocity on pressure drop across a fluidized bed reactor.

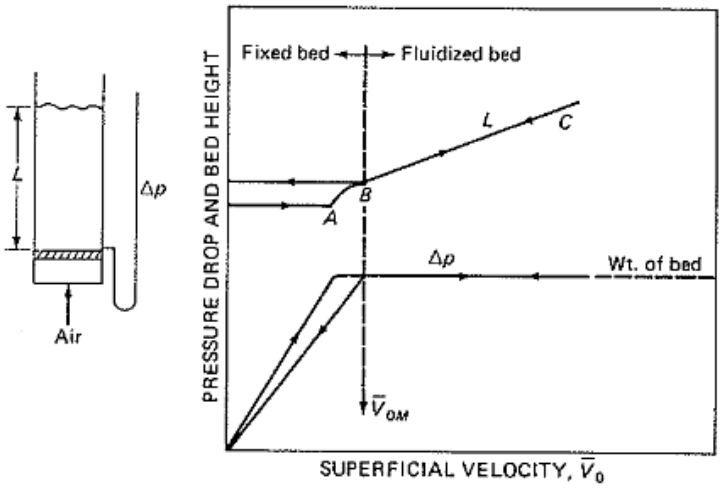

Figure 1: Effect of superficial velocity on pressure drop and bed height of a fluidized bed reactor

The requirements for this particular reactor were that the reactor be simulated in the simulation software SimSci Pro/II using an isothermal plug flow reactor. An internal heat exchanger exists inside the reactor that provides the isothermal capabilities. The reactor operating temperature is constrained by the operating range of the catalyst. The same design constraints for the Unit 500 reactor applied to the fluidized bed reactor. The Unit 500 reactor temperature constraints were a maximum operating temperature of 1000 K with a maximum of 50 K variation in temperature over the length of the reactor. The pressure constraint for the reactor was an operating pressure in the range of 0.75 to 2.5 bar. Another constraint of the reactor design was that the inlet molar composition for the fluidized bed reactor be the same as the inlet molar composition of the optimized Unit 500 reactor. This includes a steam to ethylbenzene ratio of 15.6 to 1.

Before setting up the reactor simulation, I needed to calculate the minimum fluidization velocity for this system. To find the minimum fluidization velocity, u_{mf}, I used the Wen and Yu correlation given as follows:

$$Re_{p,mf} = \frac{u_{mf} d_p \rho_g}{\mu_g} = [1135.69 + Ar]^{0.5} - 33.7 \quad (1)$$

Where $Re_{p,mf}$ is the Reynolds number; Ar is the Archimedes number, $Ar = \frac{d_p^3(\rho_s - \rho_g)\rho_g g}{\mu_g^2}$; d_p is the particle diameter; ρ_g is the density of the gas, μ_g is the gas viscosity; ρ_s is the catalyst density; and g is the acceleration due to gravity. The project statement stated that the catalyst particle diameter is 300 μm, and the density of the catalyst is 2000 kg/m^3. The optimized Pro/II flowsheet provided the values for the gas density and viscosity at operating conditions of 685°C and 190

kPa. Using these equations and values, I found the minimum fluidization velocity to be u_{mf}=0.032 m/s. The range for the superficial gas velocity for values of 3 to 10 times the minimum fluidization velocity is 0.096 to 0.320 m/s. I calculated these velocity values assuming that the gas and catalyst density and viscosity change only negligibly within the operating range for temperature and pressure. Therefore, the main constraint on the optimization was that the superficial gas velocity stays inside the range stated above. After calculating the velocity for the reactor, I verified that the pressure drop across the length of the fluidized reactor was equal to zero using the following equation:

$$\Delta P = g(1-\varepsilon)\left(\rho_s - \rho_g\right)L \qquad (2)$$

Where ΔP is the pressure drop across the reactor, g is acceleration due to gravity, ε is the void fraction of the fluidized bed, ρ_s is the particle density, ρ_g is the gas density, and L is the length of the reactor or in this particular case the height of the fluidized bed. At the max calculated fluid velocity of u_g=0.32 and the given particle diameter of d_p=300 μm, the void fraction of the bed is equal to nearly 1. With this void fraction, the pressure drop along a fluidized bed of any length is nearly 0. This pressure drop agrees with the information displayed in Figure 1 above. After determining the velocity constraint and the pressure drop for the reactor, I began setting up the reactor simulation in order to optimize.

The first step in setting up the new reactor in Pro/II was to input the chemicals in the process and setup the reaction kinetics for the reactor. The reaction proceeds according to the following set of reactions, and the chemicals

listed under the equations along with steam are the only ones present in the process:

$$C_6H_5C_2H_5 \leftrightarrow C_6H_5C_2H_3 + H_2 \quad (1)$$

Ethylbenzene Styrene Hydrogen

$$C_6H_5C_2H_5 \rightarrow C_6H_6 + C_2H_4 \quad (2)$$

Ethylbenzene Benzene Methane

$$C_6H_5C_2H_5 + H_2 \rightarrow C_6H_5CH_3 + CH_4 \quad (3)$$

Ethylbenzene Hydrogen Toluene Methane

After entering the chemicals into the process simulator and setting up the reaction kinetics, I chose a thermodynamic package to carry out the calculations for the simulator. The thermodynamic model selected to calculate solutions in a process simulator is extremely important, and choosing the wrong model gives results that are not accurate or useful. I chose the SRK SimSci package as the model for this reactor. This thermodynamic model uses the Soave-Redlich-Kwong equation of state to make thermodynamic calculations. I found a suitable thermodynamic package by analyzing the process using Figure 1.

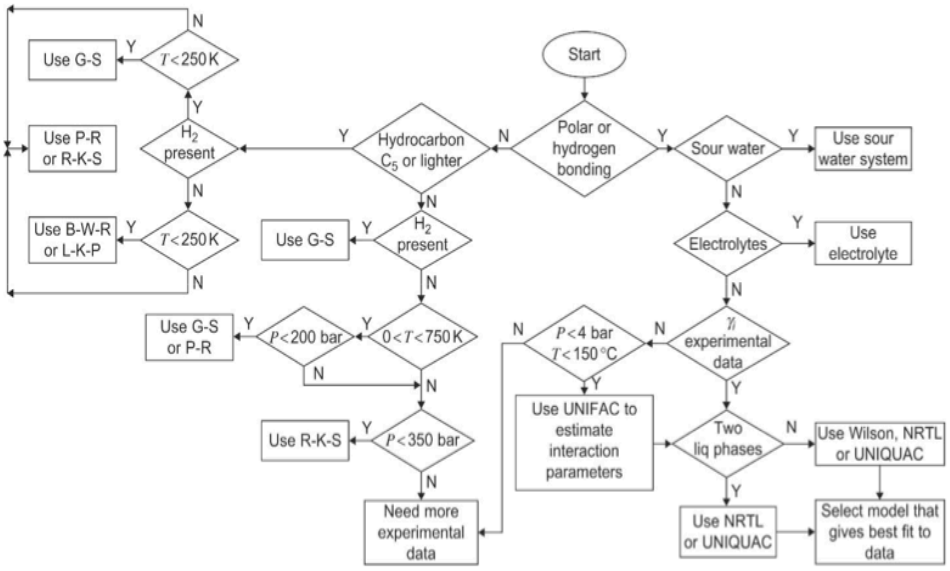

Figure 2: Guidelines for Selection of Thermodynamic Package

In the styrene production process, no polar or hydrogen bonding is present; hydrocarbons with greater than five carbons exist in the process; molecular hydrogen is present in the process, and the temperature of the process is greater than 250 K. Following Figure 1 as a guideline the SRK SimSci package proved to be a correct choice.

In order to begin the optimization and design of the reactor, I set up the process flowsheet for the reactor. As mentioned earlier, the reactor chosen for this project was a fluidized bed isothermal plug flow reactor. Fluidized bed reactors have a bubbling nature. In order to compensate for bubbling in the reactor, simulation of the reactor requires that some of the feed gas bypass the catalyst in the reactor. The reactor simulation required a feed gas bypass of 10%. With a 10% feed gas bypass the single-pass conversion in the reactor can only reach a maximum

conversion of 90%. The bypass stream must have a heat exchanger and a valve added to it in order to be able to match the temperature and pressure in the reactor outlet stream when it recombines.

During the flowsheet setup, I specified the inlet stream properties and the initial specifications for the reactor, heat exchanger, and valve. The molar composition of the feed stream to the reactor remained the same as the molar composition of the optimized reactor from the original optimization project. After setting up the flowsheet for the reactor, I began the actual optimization process.

The first step in optimizing the reactor was to choose an objective function for the optimization. I selected the maximum output of styrene in the stream exiting the reactor as my objective function. Since production of styrene from ethylbenzene is the objective of the original process, I decided that maximizing the styrene out of the reactor was the best way to optimize. The next step in the optimization was to select certain parameters to optimize and to define the ranges over which to vary them. The chosen parameters were the reactor inlet stream temperature and pressure, the total volume of catalyst, and the number of reactors in parallel. The only constraint entered into the optimizer was that the superficial gas velocity in the reactor remains in the range 0.096 to 0.320 m/s. The actual specifications for the reactor were that the temperature remains constant across the reactor and that no pressure drop occurs across the reactor. Another specification for the reactor was the length of the reactor or the fluidized bed height. In order to find the optimal inner diameter for the reactor, the dimension of reactor length needs to be specified in the reactor. Pro/II optimizes for reactor catalyst volume. Therefore, it is

appropriate to choose diameter or length as a specification. The value ranges for the optimization parameters were as follows: inlet temperature from 450 to 700°C, inlet pressure from 75 kPa to 250 kPa, inner diameter of 0 to 8 m, and the number of reactors from 1 to 15 reactors in parallel. A constraint of the reactor is that it cannot operate a temperature higher than 1000 K or 727°C. The pressure constraint for the reactor is that operating pressure needs to stay between 75 kPa and 250 kPa. The inner diameter range and the number of reactors range are not as intuitive. Since this reactor optimization project has no economic investment constraints, it is feasible to design an infinite number of infinitely large reactors. In order to stay within reason, I assumed a max reactor diameter of 8 m and a max number of parallel reactors of 15 in order to keep the fixed capital investment to a reasonable amount.

To get a better understanding of how each variable of the reactor affected the objective function, I performed case studies that included: the inner diameter, catalyst bed height, number of reactors, temperature, and pressure versus the production of styrene. The case studies showed that if everything else remains constant that an increase in the inner diameter for the reactor decreases the gas velocity in the reactor, and it will also decrease the yield. A larger fluidized bed height seems to lower the yield of the reactor, but it does not affect the gas velocity of the reactor if every other parameter remains constant. Increasing the number of reactors reduces the velocity, but it also reduces the yield of styrene. Case studies on the effect of temperature and pressure on the production of styrene showed that decreasing the pressure increased the yield and the velocity in the reactor and

decreasing the temperature decreased the yield and velocity of the reactor. The figures below display the effects of pressure, temperature and catalyst bed diameter on styrene production.

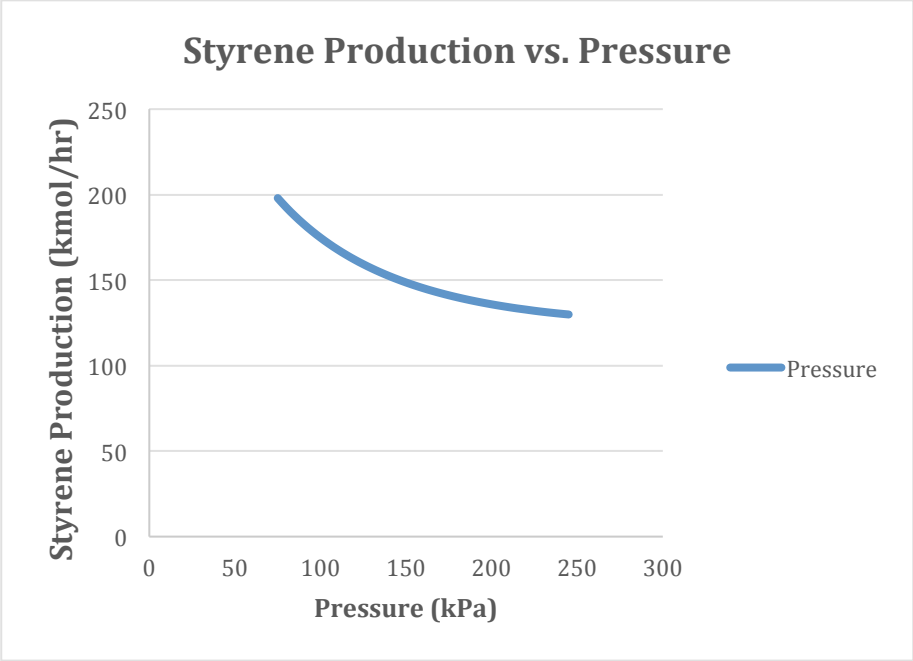

Figure 2: Display of the effect of changing reactor inlet pressure on styrene production

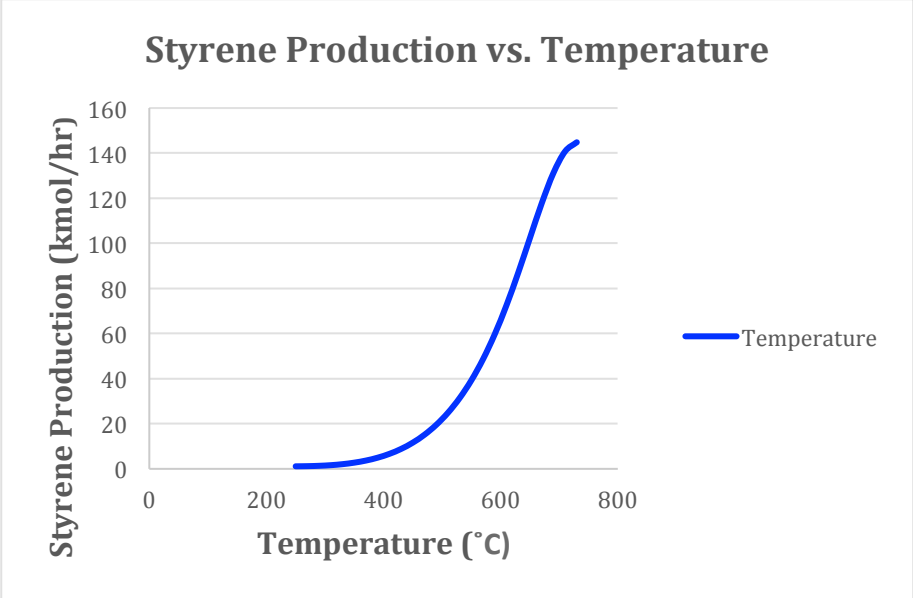

Figure 3: Display of the effect of varying reactor inlet temperature on styrene production

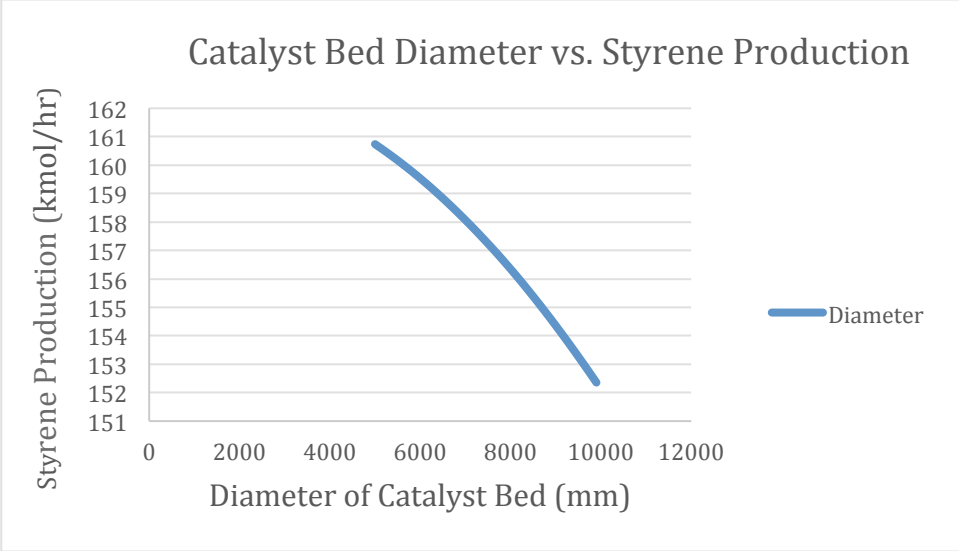

Figure 4: Display of the effect of varying catalyst bed diameter on styrene production

The process simulator contains a calculator feature that has the capability to output the results of parameter optimizations and to calculate solutions to user-defined formulas. In order to output the solutions for the optimization, I set up a

calculator to display the results of the optimizer calculations. The results displayed from the calculator were the conversion of ethylbenzene, the selectivity of ethylbenzene to styrene, the yield of styrene to ethylbenzene, and the maximum velocity of the gas inside the reactor. A second calculator displayed the height of the fluidized bed, the diameter, the total fluidized catalyst volume, the temperature, and the pressure of the reactor. The results of the optimizer confirmed the trends exhibited in the case studies. The optimized reactor system has a total fluidized catalyst bed volume of 75.4 m^3. For this volume of catalysts, the optimized system requires the employment of 15 reactors in order to keep the superficial gas velocity within the required range. The optimized reactor operates at a temperature of 715°C and a pressure of 75 kPa. The optimized reactor parameters produced a total flowrate of styrene out of the reactor system of 193 kmol/hr and yield of ethylbenzene to styrene of 68 %. The original optimized reactor produced 123 kmol/hr styrene. Therefore, the fluidized bed isothermal reactor increased the styrene production by 57%.

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Appendix:

Appendix A

Optimization of Styrene Production Process

ChE 451: Process Design

Nishal Bhikha

Wilson Look

Matt Peaster

December 12th, 2015

Executive Summary:

By performing a sensitivity analysis, we determined that changes in the raw materials, revenue, fixed capital investment (FCI), and utilities have the most impact in increasing the net present value (NPV) of the proposed process. An oversight in the base case reactor design forced us to make major modifications to our process in the reactor section resulting in an increase in raw material cost for the optimized plant. The base case pressure drop across the reactors results in an incredibly high velocity that was not accurately accounted for in the original base case design. We determined that it was necessary to have five adiabatic reactors in parallel to produce the target of 100,000 tonnes/yr of styrene.

Additionally, heat integration greatly improved the utility cost. Essentially one "hot" stream, the effluent from the reactor, needs to be cooled in preparation for the separation section. We decided to use this stream to preheat the low-pressure steam inert before it enters the fired heater. We also used the reactor effluent stream to vaporize the combined ethylbenzene feed before using cold utilities to reach the desired separation feed temperature. The heat integration for the optimized process reduced the utility cost by $12 million/yr from the base case.

Furthermore, modifications to the first distillation column allowed us to sell a purified benzene/toluene stream to increase revenue. We also lowered raw material costs by optimizing the liquid/liquid/vapor separator to reduce ethylbenzene and styrene lost in the fuel gas. Optimizations to the separation section allowed us to recycle more ethylbenzene and take more of the styrene produced to actual product without losing it to fuel gas. We are also able to sell

more fuel gas due to these changes. Optimizations to the separation section resulted in an increase of revenue of $15 million/yr. We also reduced the fixed capital investment by changing the materials of construction for various pieces of equipment. We replaced the titanium distillation columns with carbon steel distillation columns, and we also replaced stainless steel with carbon steel for a few heat exchangers. Changes in construction materials for process equipment reduced our fixed capital investment by $117 million.

Implementation of the changes mentioned above resulted in NPV of -$412 million that translates to an equivalent annual operating cost (EAOC) of $72.9 million for the optimized case. This EAOC is much lower than the projected cost of purchasing 100,000 tonnes/yr for $160 million/yr. Table 1 gives a summary of the bottom line results of optimization of the Unit 500 styrene production process.

Table 1: Bottom Line Results of Unit 500 Optimization

	Optimized Case ($M/yr)	**Base Case ($M/yr)**
Revenue	185	170
Raw Materials	-137	-118
Utilities	-57	-69
Total FCI	-136	-253
Cost of Manufacturing	-260	-278
Net Present Value	**-412**	**-558**
EAOC	**73**	**98**

Table 1 shows that changes made to the separation section increased the total revenue of the process by $15 million/yr. The raw material cost for the process actually increased in the optimized case by $19 million/yr. This increase in raw material cost was due to the fact that the base case reactor design was not possible due to the pressure drop across the reactor. We reduced the utility cost for the optimized case by $12 million/yr by integrating heat more efficiently, and changes made to the materials of construction for certain pieces of process equipment lowered the FCI cost by $117 million/yr. Overall, Table 1 illustrates that the bottom line for our optimized styrene process over the life of the project is -$412 million/yr and an EAOC of $72.9 million/yr. This optimized NPV is $146 million greater than the base case process design NPV. Even though the NPV for the base case plant is much lower than the NPV for the optimized styrene plant, we suggest that the plant needs further optimization and a more detailed estimate. We recommend optimizing the reactors further to find a reactor system with a higher yield of ethylbenzene to styrene. The separation section also needs further optimization. The liquid/liquid/vapor separator still loses some ethylbenzene and styrene to fuel gas, and further optimization may provide a solution to this problem.

Contents:

Nomenclature:

F_T- temperature correction factor

F_p- pressure factor

F_m- material factor

K_n- Constants from Turton (Table A.1)

C_n- Constant from Turton (Table A.2)

B_n- Constant from Turton (Table A.4)

Q- Duty, kW

h- Local heat transfer coefficient, W/m^2K

L- length of reactor, m

bfw- boiler feed water

cw- cooling water

lps- low pressure steam

hps- high pressure steam

A- area, m^2

V- volume, m^3

D- column diameter, m

H- column height, m

W- work, kW

N_{ol}- number of operating labor

P– pressure, kPa

ρ- density, kg/m^3

m- mass flow rate, kg/hr

mw- molecular weight

COM- cost of manufacturing, $

FCI- fixed capital investment, $

C_{TM}- total module cost, $

C_{GR}- grass roots cost, $

C_{ol}- cost of operating labor, $

Δp- pressure change across reactor, kPa

V_o-superficial velocity, m/s

ε- void fraction

Φ_s-sphericity

D_p-diameter of spherical particle

μ-viscosity, cP

t- Holdup time for sizing vessels, m

η- efficiency

ΔT_{LM}-log mean temperature difference, C°

U- overall heat transfer coefficient, W/m^2K

RM– Raw Materials, $

Ut- Utilities, $

WT- Waste Treatment, $

Introduction:

The purpose of this report is to describe the optimization of a styrene production process. Styrene polymerizes to produce polystyrene, which is a lightweight substance with a variety of industrial uses such as packaging, foam insulation, and food containers (1). Production of styrene occurs from the dehydrogenation of ethylbenzene as seen in Equations 1 through 4. The styrene production process, Unit 500, discussed in this report is only a portion of a larger plant that manufactures benzene, ethylbenzene, and polystyrene. The process concept diagram in Figure 1 illustrates a simplified version of the styrene process in Unit 500.

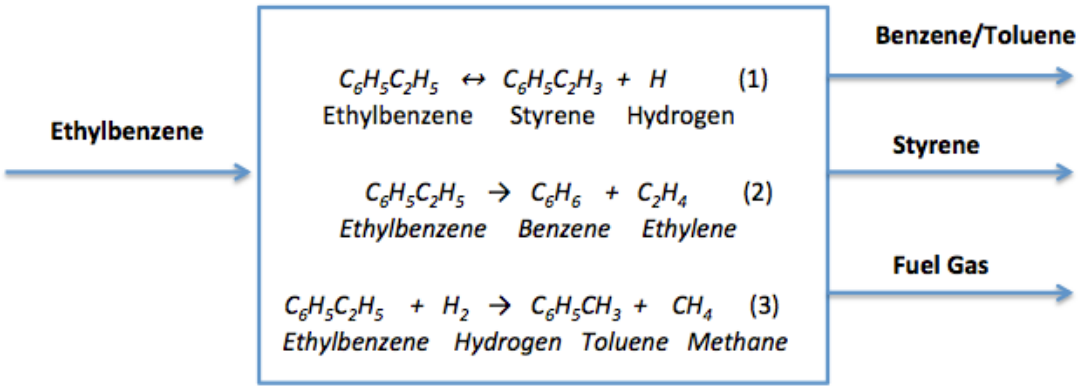

Figure 1: Process Concept Diagram of the Production of Styrene

As illustrated in Figure 1, ethylbenzene reacts in a reversible reaction to produce styrene and hydrogen. Two undesired side reactions take place in the process. In the first undesired reaction ethylbenzene reacts to produce benzene and ethylene, and in the second undesired reaction ethylbenzene reacts with hydrogen to produce toluene and methane. The only raw material needed for the Unit 500 styrene production process is ethylbenzene. Figure 1 shows that the reacted ethylbenzene

produces three separate sellable products in the process. These products are a benzene/toluene mixture, fuel gas, and the desired product styrene. Since production of styrene is the goal of the process and the most profitable product of the ethylbenzene reactions, the main objective of the optimization of the process is to maximize the yield of ethylbenzene to styrene and to optimize the separation of the product components from unreacted ethylbenzene.

Initially, we calculated an economic potential, as seen in Table 2, for the process in order to get an idea of the potential revenue of the process. The economic potential calculation assumes that all components separate perfectly and that we can sell all products. Table 2 illustrates that the process buys 136 kmol/hr of ethylbenzene, and it produces and sells 120 kmol/hr of styrene, 113 kmol/hr of hydrogen, 8 kmol/hr of benzene and toluene, and 7 kmol/hr of Methane and ethylene. From this economic potential calculation in Table 2, we see that this process has the potential to produce $8,830 dollars/hr with perfect separation and the ability to sell all products. Since the process proved to be profitable, we decided to proceed with optimization.

Table 2: Economic Potential of Styrene Production Process

Components	Flow Rate	Value		Density	Molar Mass	Total Cost/Revenue
Pure	(kmol/hr)	($/kg)	(BTU/lbmol)	(kg/m^3)	(kg/kmol)	($/hr)
Ethylbenzene	136	0.900	-	866.0	106	-12,950
Styrene	120	1.598	-	909.0	104	19,975
Hydrogen	113	-	51,600	0.099	2	305
Benzene	8	0.919	-	876.5	78	576
Toluene	8	1.033	-	866.5	92	764
Methane	7	-	21,400	-	16	59
Ethylene	7	-	20,500	-	28	99
Economic Potential ($/hr)						
8,830						

The main objective of optimization was to maximize the NPV of the process while satisfying a set of given constraints that mainly include the production requirements for styrene and the reactor and separation section operating temperatures. The production requirement for Unit 500 is 100,000 tonnes/yr of styrene of 99.5 wt% purity. The reactor designed to produce the styrene must not have temperature that exceeds 1000 K, and the temperature drop across the reactor cannot be greater than 50 K. After the reactor, the styrene produced has some specific constraints in the separation section. In order to prevent the polymerization of styrene in the separation section, the temperature must remain below 125°C. Table 3 summarizes the economic constraints for the project.

Table 3: Economic Parameters for the Styrene Project

Parameters	Value
Operating Labor Cost	$59,580 per operator per year
Corporate Tax Rate	35%
Depreciation Method	7 year MACRS
MARR	12%
Operating Hours Per Year	8000

When designing the optimized styrene case, we assumed our entire process operated at steady state. To simplify our heat exchanger calculations, we assumed that the temperature correction factor is 0.9 with no phase change and 1 for phase change.

Before beginning optimization, we performed a sensitivity analysis on the process. The results of the sensitivity analysis indicated that changes in raw materials, revenue, utilities, and FCI most effectively maximize the NPV.

We started the optimization by focusing the reactor to increase the yield of raw material to product. In order to more efficiently use raw materials and increase revenue, we optimized the separation section to more effectively separate ethylbenzene from our products. After optimizing the reactor and separation sections, we addressed the utility costs by integrating heat in order to find the most economical use of energy in the process. Finally, we researched the construction materials of the process equipment and made the appropriate changes to reduce the FCI

Results:

Figure 2: Process Flow Diagram for the Optimized Plant

Table 4: Stream Tables for Unit 500 Styrene Optimized Plant[1]

Stream No.	1	2	3	4	5	9
Temperature (ºC)	136	107	350	160	830	685
Pressure (kPa)	210	200	180	600	550	190
Vapor Mole Fraction	0	0	1	1	1	1
Total Flow (kg/hr)	18,400	56,300	56,300	148,000	148,000	204,000
Total Flow (kmol/hr)	174	531	531	8,210	8,210	8,741
Comp Flow (kmol/hr)						
Water				8,210	8,210	8,210
Ethylbenzene	170	526	526			526
Styrene		1.21	1.21			1.21
Hydrogen						
Benzene	1.74	1.74	1.74			1.74
Toluene	1.74	1.85	1.85			1.85
Ethylene						
Methane						

Stream No.	10	11	12	13	14	15
Temperature (ºC)	653	465	361	270	170	51
Pressure (kPa)	160	145	125	110	80	120
Vapor Mole Fraction	1	1	1	1	1	0.02
Total Flow (kg/hr)	204,000	204,000	204,000	204,000	204,000	204,000
Total Flow (kmol/hr)	8,880	8,880	8,880	8,880	8,880	8,880
Comp Flow (kmol/hr)						
Water	8,210	8,210	8,210	8,210	8,210	8,210
Ethylbenzene	364	364	364	364	364	364
Styrene	123	123	123	123	123	123
Hydrogen	100	100	100	100	100	100
Benzene	20.4	20.4	20.4	20.4	20.4	20.4
Toluene	23.9	23.9	23.9	23.9	23.9	23.9
Ethylene	18.7	18.7	18.7	18.7	18.7	18.7
Methane	22	22	22	22	22	22

[1] These tables contain rounded values to increase readability. If the component molar flow rate is 0, then trace amounts of the component actually exist.

Table 4: Stream Tables for Unit 500 Styrene Optimized Plant Cont.

Stream No.	16	17	18	20	21	22
Temperature (°C)	50.8	50.8	50.8	50.8	63.4	116
Pressure (kPa)	105	105	105	65	35	55
Vapor Mole Fraction	1	0	0	0.0004	0	0
Total Flow (kg/hr)	2,420	54,300	147,500	54,300	1,170	50,500
Total Flow (kmol/hr)	170	527	8,185	527	13	478
Comp Flow (kmol/hr)						
Water	21	4.95	8,185	4.95	0.03	
Ethylbenzene	5.50	358	0	358	1.04	356
Styrene	1.58	121	0	121	0.15	121
Hydrogen	99.6	0.12	0	0.12		
Benzene	1.99	18.4	0	18.4	3.28	
Toluene	0.94	22.9	0	22.9	8.49	0.11
Ethylene	18.0	0.66		0.66	0	
Methane	21.7	0.28	0	0.28	0	

Stream No.	23	24	26	27	28	29
Temperature (°C)	90.8	124	63.4	124	50.8	92.6
Pressure (kPa)	25	55	200	200	200	210
Vapor Mole Fraction	0	0	0	0	0	0
Total Flow (kg/hr)	37,900	12,600	1,170	12,600	37,900	148,000
Total Flow (kmol/hr)	357	121	13	121	8,185	357
Comp Flow (kmol/hr)						
Water			0.03		8,184	
Ethylbenzene	356	0.59	1.04	0.59	0.10	356
Styrene	1.21	120	0.15	120	0	1.21
Hydrogen					0	
Benzene			3.28		0.01	
Toluene	0.11		8.49		0.05	0.11
Ethylene			0			
Methane			0		0.03	

Table 4: Stream Tables for Unit 500 Styrene Optimized Plant Cont.

Stream No.	30	31	32	33	34
Temperature (ºC)	455	829	352	194	216
Pressure (kPa)	585	229	200	95	135
Vapor Mole Fraction	1	1	1	1	1
Total Flow (kg/hr)	148,000	148,000	56,300	204,000	204,000
Total Flow (kmol/hr)	8,210	8,210	531	8,880	8,880
Comp Flow (kmol/hr)					
Water	8,210	8,210		8,210	8,210
Ethylbenzene			526	364	364
Styrene			1.21	123	123
Hydrogen				100	100
Benzene			1.74	20.4	20.4
Toluene			1.85	23.9	23.9
Ethylene				18.7	18.7
Methane				22	22

Stream No.	35	36	37	38	39
Temperature (ºC)	63.4	54.8	120	55	172
Pressure (kPa)	35	35	105	90	240
Vapor Mole Fraction	1	1	1	1	1
Total Flow (kg/hr)	2,700	5,120	5,120	5,120	5,120
Total Flow (kmol/hr)	36.2	207	207	207	207
Comp Flow (kmol/hr)					
Water	4.92	25.9	25.9	25.9	25.9
Ethylbenzene	0.75	6.24	6.24	6.24	6.24
Styrene	0.09	1.68	1.68	1.68	1.68
Hydrogen	0.12	100	100	100	100
Benzene	15.1	17.1	17.1	17.1	17.1
Toluene	14.3	15.2	15.2	15.2	15.2
Ethylene	0.66	18.7	18.7	18.7	18.7
Methane	0.28	22	22	22	22

Table 5: Partial Equipment Summary Unit 500 Styrene Optimized Plant

Heat Exchangers

E-511 A= 585 m^2 1-2 exchanger, fixed tube sheet, 316 SS Q= 47.567 GJ/hr Shell side pressure – 200 kPa Tube side pressure – 145 kPa Price: $1,600,000	**E-512** A= 832 m^2 1-2 exchanger, floating head, 316 SS Q= 90.4035 GJ/hr Shell side pressure – 600 kPa Tube side pressure – 160 kPa Price: $3,400,000
E-513 A= 889 m^2 1-2 exchanger, fixed tube sheet, Carbon Steel Q= 38.6456 GJ/hr Shell side pressure – 4200 kPa Tube side pressure – 125 kPa Price: $1,220,000	**E-514** A= 682 m^2 1-2 exchanger, fixed tube sheet, Carbon Steel Q= 36.5574 GJ/hr Shell side pressure – 1100 kPa Tube side pressure – 110 kPa Price: $1,540,000
E-515 A= 603 m^2 1-2 exchanger, fixed tube sheet, Carbon Steel Q= 424.653 GJ/hr Shell side pressure – 600 kPa Tube side pressure – 95 kPa Price: $900,000	**E-516** A= 880 m^2 1-2 exchanger, fixed tube sheet, Carbon Steel Shell side pressure – 200 kPa Tube side pressure – 135 kPa Price: $2,850,000
E-517 A= 306 m^2 1-2 exchanger, floating head, Carbon Steel Shell side pressure – 200 kPa Tube side pressure – 35 kPa Price: $308,000	**E-518** A= 356 m^2 1-2 exchanger, fixed tube sheet, Carbon Steel Shell side pressure – 600 kPa Tube side pressure – 55 kPa Price: $440,000
E-519 A= 786 m^2 1-2 exchanger, floating head, Carbon Steel Shell side pressure – 200 kPa Tube side pressure – 25 kPa Price: $530,000	**E-520** A= 756 m^2 1-2 exchanger, floating head, Carbon Steel Shell side pressure – 600 kPa Tube side pressure – 55 kPa Price: $850,000
E-521 A= 117 m^2 1-2 exchanger, floating head, Carbon Steel Shell side pressure – 200 kPa Tube side pressure – 105 kPa Price: $220,000	

Reactors

R-511 316 stainless steel packed bed Void fraction = 0.5 Volume = 126 m^3 Price: $20,300,000

Table 5: Partial Equipment Summary Unit 500 Styrene Optimized Plant Cont.

Fired Heater

H-511 Fire heater – refractory lined, stainless steel tubes required heat load = 124.25 GJ/hr 80% thermal efficiency maximum pressure rating of 600 kPa Price: $13,000,000	

Vessels

V-511 Carbon Steel Maximum operating pressure = 200 kPa Vertical Height = 7.44 m Diameter = 2.48 m Volume = 36 m^3 Price: $310,000	**V-512** Carbon Steel Horizontal L/D = 3 V = 13.2 m^3 Price: $92,000
V-513 Carbon Steel Horizontal L/D = 3 V = 51.8 m^3 Price: $218,000	

Towers

T-511 Carbon Steel 38 Sieve Trays 65% efficient trays Feed on tray 6 0.5 meter tray spacing column height = 22 m diameter = 4.53 m maximum pressure rating of 100 kPa Price: $4,100,000	**T-512** Carbon Steel 122 Sieve Trays 65% efficient trays Feed on tray 31 0.4 meter tray spacing column height = 53 m diameter = 8.37 m maximum pressure rating of 100 kPa Price: $68,000,000

Table 5: Partial Equipment Summary Unit 500 Styrene Optimized Plant Cont.

Compressors and Drives

C-511 Carbon Steel Actual W = 104 kW 76% adiabatic efficiency Price: $280,000	**C-512 A-C** Carbon Steel Actual W = 2,182 kW 76% adiabatic efficiency Price: $9,850,000
C-513 Carbon Steel Actual W = 248 kW 76% adiabatic efficiency Price: $614,000	**C-514** Carbon Steel Actual W = 210 kW 76% adiabatic efficiency Price: $530,000
D-511 A/B Electric/Explosion Proof Actual W = 116 kW 90% efficiency Price: $310,000	**D-512 A-C/D-F** Electric/Explosion Proof Actual W = 2,424 kW 90% efficiency Price: $3,530,000
D-513 A/B Electric/Explosion Proof Actual W = 276 kW 90% efficiency Price: $525,000	**D-514 A/B** Electric/Explosion Proof Actual W = 233 kW 90% efficiency Price: $621,000

Pumps

P-511 A/B Carbon steel – centrifugal Actual Power = 5.74 kW Efficiency 70% Electric Drive Price: $70,500	**P-512 A/B** Carbon steel – centrifugal Actual Power = 1 kW Efficiency 70% Electric Drive Price: $47,000
P-513 A/B Carbon steel – centrifugal Actual Power = 1 kW Efficiency 70% Electric Drive Price: $47,000	**P-514 A/B** Carbon steel – centrifugal Actual Power = 1 kW Efficiency 70% Electric Drive Price: $47,000
P-515 A/B Carbon steel – centrifugal Actual Power = 1 kW Efficiency 70% Electric Drive Price: $47,000	**P-516 A/B** Carbon steel – centrifugal Actual Power = 5.34 kW Efficiency 70% Electric Drive Price: $257,000

Table 6: Utility Summary for Unit 500

E-512	E-513	E-514	E-515	E-516
lps	bfw→hps	bfw→mps	bfw→lps	cw
148,000 kg/hr	16,000 kg/hr	13,000 kg/hr	4,030 kg/hr	10,400,000 kg/hr

E-517	E-518	E-519	E-520	E-521
lps→bfw	cw	lps→bfw	cw	cw
16,600 kg/hr	645,000 kg/hr	42,700 kg/hr	2,170,000 kg/hr	20,600 kg/hr

Illustrated above in Figure 2 is a process flow diagram of the optimized process followed by stream tables in Table 4, a partial equipment summary in Table 5, and utility summary in Table 6. As stated in the introduction, the optimization of the styrene production process began by performing an economic sensitivity analysis on the base case as illustrated below in Figure 3.

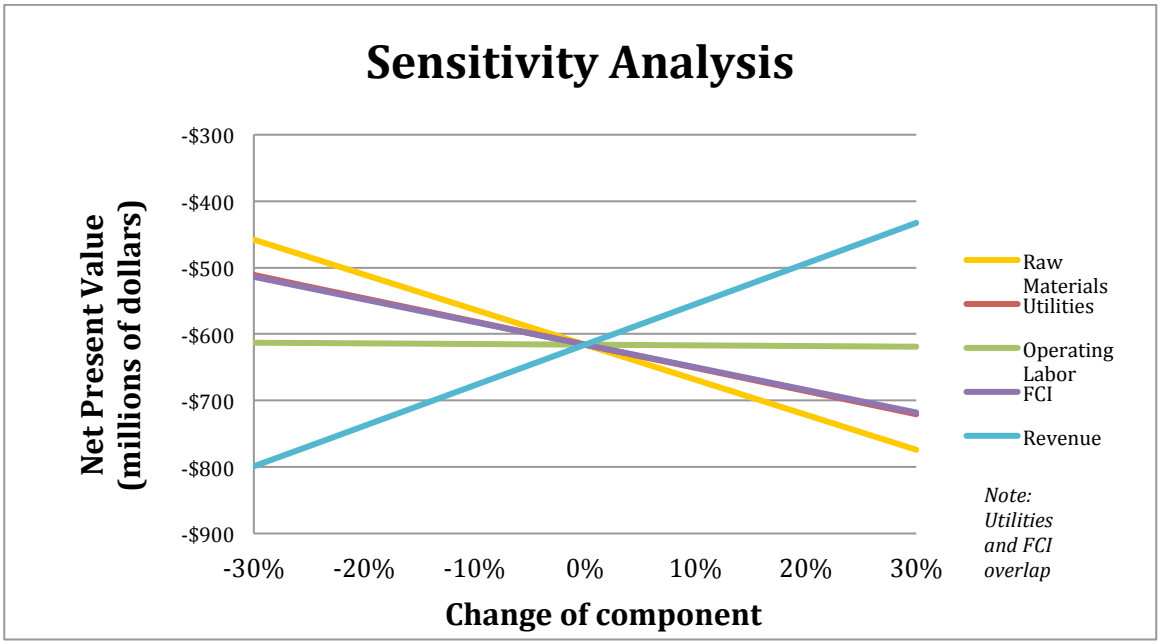

Figure 3: Sensitivity Analysis of Unit 500 Styrene Process

The data shown in Figure 3 indicates how changes in the listed areas affect the NPV. Optimization began by addressing the most sensitive areas first. Since the plant has a required yearly production of 100,000 tonnes/yr of styrene, the revenue from styrene cannot change. As illustrated in Figure 3, the area most sensitive to changes is the raw material cost followed by the utility cost and the fixed capital investment cost. In order to address the sensitivity of the process to changes in raw materials, we began optimization by first focusing on the reactor and optimizing for increased yield of ethylbenzene to styrene. Following the reactor optimization, we optimized the utilities for the process. Utility cost was the second most sensitive to change as seen in Figure 3. We reduced the utility cost by using the hot process stream from the reactor to heat the low-pressure steam before it entered the fired heater. Finally, we analyzed the possibility of changing some of the process equipment's material of construction in order to try and reduce the FCI. The separation section was all stainless steel in the base case, and research on construction materials showed that carbon steel is an appropriate and less expensive alternative to stainless steel for this application. This material change reduced the FCI.

We used the SimSci PRO/II simulation software to model our process to aid optimization. The first step in setting up a PRO/II simulation is selecting an appropriate thermodynamic model. We used Figure 4 to analyze our process and arrive at a suitable model.

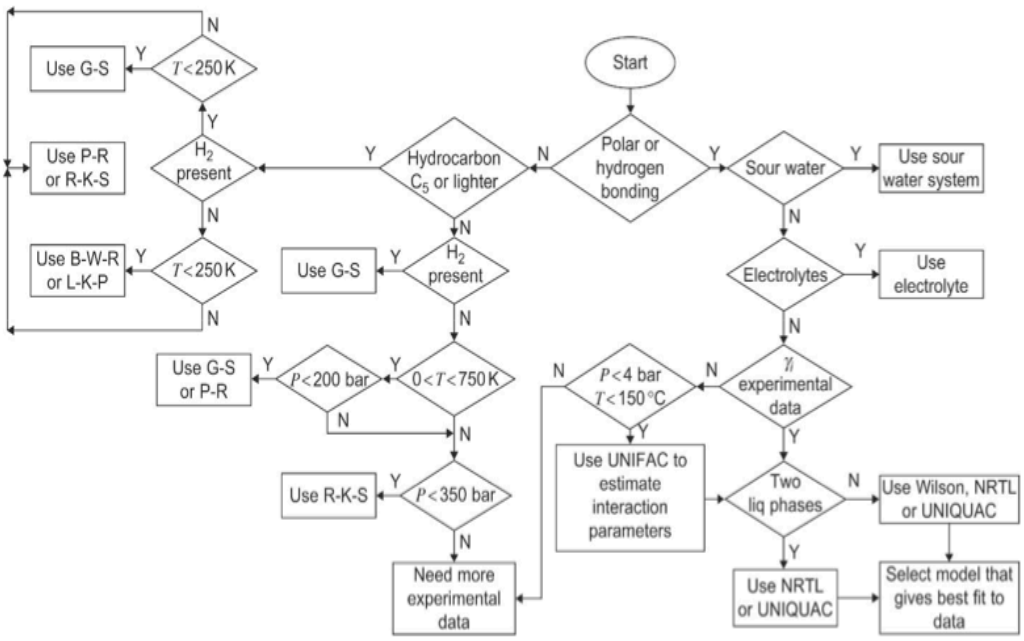

Figure 4: Guidelines for Selection of Thermodynamic Package in Pro/II

In the styrene production process no polar or hydrogen bonding is present; hydrocarbons with greater than five carbons exist in the process; hydrogen is present in the process; and the temperature for the process is greater than 250 K. These conditions led to the choice of the SRK SIMSCI thermodynamic package. The SRK package uses the Soave-Redlich-Kwong equation of state to make thermodynamic calculations. All of process on the front end feed section uses the SRK package for one liquid phase. The heat exchanger E-516 and the flash vessel V-511 use the two liquid phase SRK package. After being compressed in C-512, Stream 34 has a liquid organic phase and a liquid water phase. Therefore, the two liquid phase SRK package is most appropriate for E-516 and V-511. It is important to note that the separation of ethylbenzene and styrene is somewhat difficult to model due

to the similarities between the components. As such, we applied the Ideal package to our second distillation column and styrene pump.

The objective of the reactor optimization was to design a reactor that gives the greatest yield of ethylbenzene to styrene. We investigated the optimization of an adiabatic and isothermal plug flow reactor. We determined that the process required at least five parallel reactors to keep the velocity of the system in a possible range without having choked flow. For this reason the raw material cost for ethylbenzene increased from the base case to the optimized case. The base case failed to take the velocity into account thus delivering an impractical scenario. An economic analysis on both the isothermal and adiabatic plug flow optimized reactors, illustrated in Table 7, indicated that the adiabatic set had the potential to provide greater profit. This result prompted our team to proceed optimizing the process using the adiabatic plug flow reactors.

Table 7: **Economic Analysis Comparing Isothermal and Adiabatic Reactors**

	Isothermal	**Adiabatic**
Feed into Reactor (kmol/hr)	7,345	8,986.5
EB Feed into Reactor (kmol/hr)	442.5	541.2
Styrene Produced (kmol/hr)	120.5	120.5
Recycle Ethylbenzene (kmol/hr)	222.8	356.3
Recycle Styrene (kmol/hr)	1.05	1.484
Recycle Toluene (kmol/hr)	0.2555	0.197
Extra Fired Heater (GJ/hr)	17.5	
Economic Analysis:		
Styrene Produced ($M/yr)	160.5	160.5
Ethylbenzene Buy ($M/yr)	-168	-141.3
Extra Fire Heater Cost ($M/yr)	-1.55	
Net Profit ($M/yr)	-7.55	19.2

The objective of the feed section design was to satisfy the optimized reactor's required inlet conditions. Optimization of the reactor showed that Stream 9 must have a steam to ethylbenzene ratio of 15.6, a temperature of 685 ˚C, and a pressure of 190 kPa.

In the separation section, we analyzed multiple distillation towers and liquid/liquid/vapor separator specifications. We determined that increasing the pressure to 120 kPa and lowering the temperature to 51˚C in Stream 15 reduced the amount of ethylbenzene and styrene lost to the fuel gas stream. This allowed the process to recycle more ethylbenzene and to take more of the styrene produced in the reactor to actual product. Furthermore, modifications to T-511 allowed us to produce a 90 mol% benzene/toluene stream to be sold to increase revenue. These modifications to T-511 included reducing the top tray pressure and temperature to 35 kPa and 63.4 ˚C respectively. The number of actual trays was reduced to 38 with a tray efficiency of 65%. The changes made to the separation section increased the total revenue for the process by $15 million/yr.

After concluding the optimization of the separation section, we integrated heat in order to reduce utility costs. The process needs heat to drive the reaction. After the reaction, the process stream needs cooling in order to separate and prevent the polymerization of styrene. With this in mind, we chose to use the reactor effluent instead hot utilities to preheat the low-pressure steam feed and the combined ethylbenzene feed. The reactor effluent, Stream 10, heats the low-pressure steam in E-512 to a temperature of 455 ˚C before it enters the fired heater. This reduces the required duty and fuel gas cost for the H-511 by more than 50%.

After preheating the low-pressure steam, the process stream leaving E-512, Stream 11, heats the combined ethylbenzene feed stream in E-501 to 350 ˚C. A series of heat exchangers then cools the process stream to 51˚C leading to the separation section. These changes in heat integration reduced the utility cost by $12 million/yr.

We also investigated the materials of construction. Research on the nature of hydrogen embrittlement and corrosive materials in metals showed that carbon steel is a suitable material for our process (2) (3) (4). Hydrogen embrittlement occurs when monoatomic hydrogen is present. This monoatomic hydrogen can seep into the metal of the process equipment and create a small pressure pocket. Over time as more and more hydrogen settles in this pocket, cracks occur which challenge the integrity of the equipment. Stainless steel is resistant to hydrogen embrittlement. Monoatomic hydrogen is only present in R-511 for this process. Therefore, R-511 material is stainless steel (2) (3) (4). Figure 5 shows the temperature constraints for stainless steel, and Figure 6 shows the temperature limitations of carbon steel. In Figure 5 and Figure 6 the maximum allowable stress is the maximum working pressure of the material, and this pressure is a function of the operating temperature of the process equipment. The operating temperatures in carbon steel vessels needs to remain below 400 °C in order to maintain integrity as seen in Figure 6. E-511 and E-512, which operate at temperatures of 455 °C and 656 °C respectively, need stainless steel construction which maintains stress integrity with operating temperatures up to almost 700 °C as seen in Figure 5. Since T-511 and T-512 have no monoatomic hydrogen present and the operating temperatures are

relatively low, carbon steel is a good choice of construction material instead of titanium. We chose these materials instead of titanium because the increased corrosion resistance is unnecessary in this case. The changes in materials of construction reduced the FCI by $117 million.

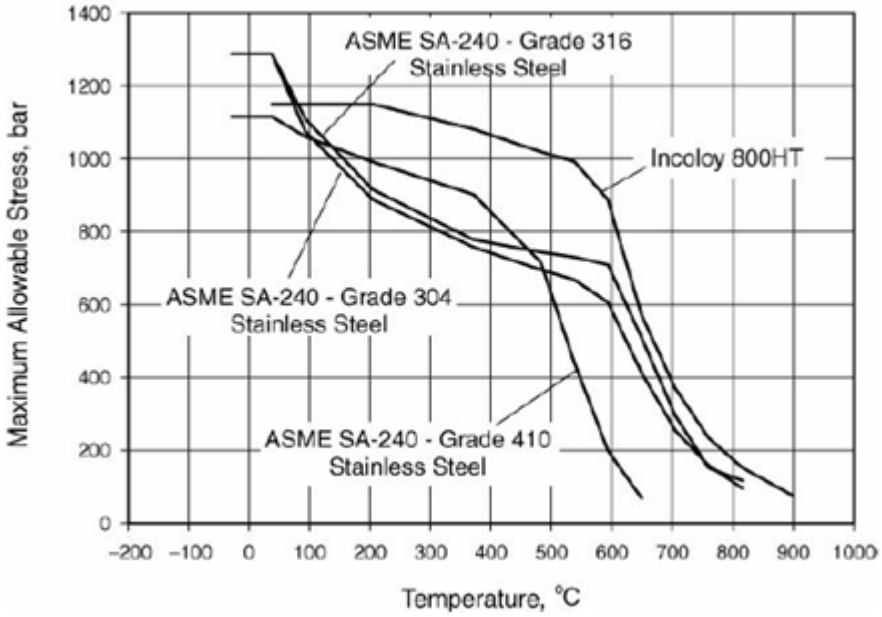

Figure 5: Maximum Allowable Stress for Stainless Steel (3)

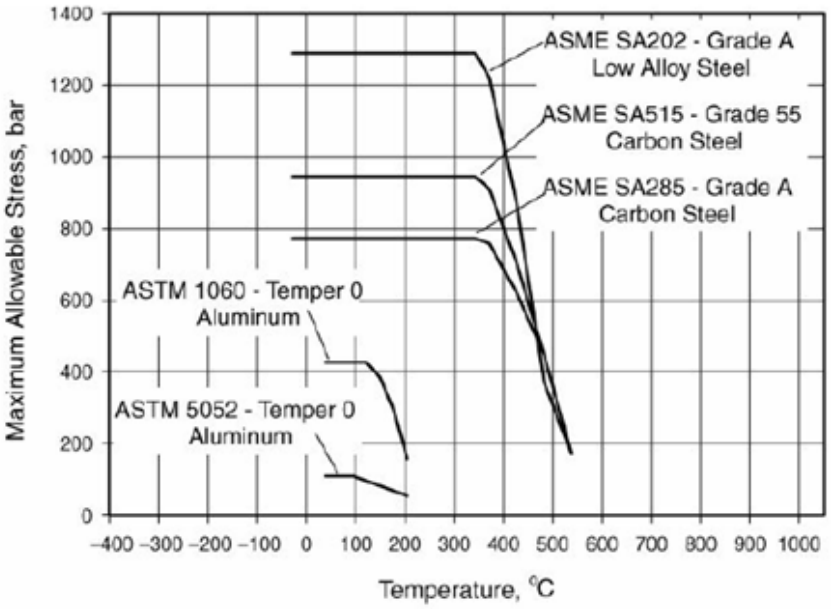

Figure 6: Maximum Allowable Stress for Carbon Steel (3)

The calculation for the total cost of manufacturing (COM) without depreciation is:

$$COM = 0.18FCI + 2.73C_{OL} + 1.23(Ut + RM + WT) \quad \textbf{(5)}$$

Table 8 shows the components included in the COM calculation. Table 9 shows a summary of components for the FCI, and Table 10 shows the utility cost by type for our plant.

Table 8: Cost of Manufacturing Summary for Optimized Unit 500

Component	Cost ($M)
Raw Materials	132.5
Waste Water	0.07
Utilities	56.5
Fixed Capital Investment	135.5
Operating Labor	0.89
Cost of Manufacturing	**259**

Table 7 gives a description of total cost of manufacturing for the optimized styrene process. The cost of manufacturing takes into account the fixed capital investment for the process along with any recurring costs for the process. Although the fixed capital investment for the process is not a recurring cost, the raw materials, wastewater treatment, utilities, and operating labor are all recurring yearly costs. The wastewater treatment and operating labor cost did not change from the base case to the optimized case for the plant. The raw material cost increased while the utility cost and the fixed capital investment decreased. The overall cost of manufacturing, as seen in Table 8, is $259 million. This COM is an $18 million decrease from the base case.

Table 9: Summary of Fixed Capital Investment for Optimized Unit 500

Unit	Price ($K)
Heat Exchangers	$13,800
Pumps	312
Reactors	20,300
Towers	71,600
Vessels	617
Compressors	11,500
Drives	4,990
Fired Heater	12,700
Total	**$135,500**

From Table 9 it is apparent that the distillation towers and reactor make up make up a large portion, 67%, of the fixed capital investment. Heat exchangers, compressors, and the fired heater contribute 28% to the total FCI. Pumps, vessels, and drives for the compressors contribute to the rest of FCI. Optimization of the towers and changes in the construction materials of some of the plant equipment

gave an FCI of $135.5 as seen in Table 9. This is an $117 million decrease from the base case.

Table 10: Utility Cost by Type for Optimized Unit 500

Utility	Electric Power (kW)	High Pressure Steam (kg/hr)	Medium Pressure Steam (kg/hr)	Low Pressure Steam (kg/hr)	Cooling Water (kg/hr)	Fuel Gas (GJ/hr)	Boiler Feed Water (kg/hr)
Totals	7,910	-16,040	-13,075	203,000	13,200,000	124.25	-26,200
Total Yearly Cost ($K/yr)	311	(3,850)	(3,095)	47,600	1,560	11,000	(514)
						Total	**$M 56.5**

Table 10 gives a summary of the total utility cost for Unit 500. Drastic reduction of the fuel gas cost due to heat integration decreased the utility cost for the plant. Optimization of the reactor along with changes in the feed section setup allowed us to reduce the total amount of low-pressure steam needed for the process. This helped to reduce the utility cost as well. The total optimized plant utility cost of $56.5 million/yr is a $12 million/yr decrease from the base case.

Process Description:

Fresh 98 mol% ethylbenzene with 1 mol% Benzene and 1 mol% toluene, Stream 1, combines with recycled ethylbenzene, in Stream 29, as Stream 2. A heat exchanger, E-511, heats Stream 2 from 107°C and 200 kPa to 350°C and 180 kPa using the reactor effluent from E-512. The heated stream, Stream 3, is compressed via a compressor C-511 to 352°C and 200 kPa. Low-pressure steam is fed to the process as Stream 4 and heated from 160°C and 600 kPa to 455°C and 585 kPa in a heat exchanger, E-512, by the hot reactor effluent, Stream 10. The steam leaving E-512, Stream 30, is further heated in a fired heater, H-511, to 830°C and 550 kPa. Superheated steam exiting H-511, Stream 5, is fed to a valve. Stream 31 exits the valve at 829°C and 229 kPa and combines with Stream 32, the stream leaving C-511. The resulting vapor mixture, Stream 9, is fed to five parallel adiabatic plug flow reactors, R-511 A-E, at 685°C and 190 kPa. The ethylbenzene fed to the reactor reacts catalytically according to the following reactions:

$$\underset{\text{Ethylbenzene}}{C_6H_5C_2H_5} \leftrightarrow \underset{\text{Styrene}}{C_6H_5C_2H_3} + \underset{\text{Hydrogen}}{H_2} \quad (1)$$

$$\underset{\textit{Ethylbenzene}}{C_6H_5C_2H_5} \rightarrow \underset{\textit{Benzene}}{C_6H_6} + \underset{\textit{Methane}}{C_2H_4} \quad (2)$$

$$\underset{\textit{Ethylbenzene}}{C_6H_5C_2H_5} + \underset{\textit{Hydrogen}}{H_2} \rightarrow \underset{\textit{Toluene}}{C_6H_5CH_3} + \underset{\textit{Methane}}{CH_4} \quad (3)$$

The reactor effluent, Stream 10, exits at 653°C and 160 kPa and is used to heat the low-pressure steam in E-512. The process stream exiting E-512, Stream 11,

is fed to E-511 at 465°C and 145 kPa. After being cooled, Stream 12 exits E-511 at 361°C and 125 kPa and is sent through a series of heat exchangers. The first heat exchanger, E-513, cools Stream 12 to 270°C and 110 kPa by vaporizing boiler feed water to produce high-pressure steam. The cooled stream exiting E-513, Stream 13, enters a second heat exchanger, E-514. Boiler feed water in E-514 cools Stream 13 to 194°C and 95 kPa and creates medium pressure steam. The stream exiting E-514, Stream 33, is fed to a third heat exchanger, E-515, where the product stream is cooled to 170°C and 80 kPa using boiler feed water to create low pressure steam. The resulting stream, Stream 14, is compressed to a pressure of 135 kPa and a temperature 216°C in a compressor, C-512. The stream exiting C-512, Stream 34, enters another heat exchanger, E-516, which cools the stream to 51°C and 120 kPa using cooling water. The stream exiting E-516, Stream 15, is fed to a liquid/liquid/vapor separator, V-511. The water rich stream leaving V-511 is pumped, via P-511, to a pressure of 200 kPa, and is sent out of the process to treatment as waste.

The organic liquid stream leaving V-511 enters a valve at a temperature of 51 and a pressure of 105 kPa. The stream exiting the valve, Stream 20, is fed to a distillation column, T-511, at a pressure of 65 kPa and a temperature of 51°C. T-511 contains 38 actual sieve trays and operates with a top tray pressure of 35 kPa and a bottom tray pressure of 55 kPa. The overhead noncondensable vapor stream from the column mixes with Stream 16, the vapor stream from V-511. The resulting stream, Stream 36, is compressed from 35 kPa and 55°C to 105 kPa and 120°C in a compressor, C-513. The stream exiting C-513, Stream 37, is sent to a heat

exchanger, E-521, where it is heated to 55°C and 90 kPa. The resulting stream, Stream 38, is sent to a second compressor, C-514, where it is compressed to 240 kPa and 169°C and is sold as fuel gas. The overhead vapor stream from T-511 is condensed using cooling water in, E-518, and the condensate is collected in the reflux drum, V-512. The liquid stream leaving T-511 is fed to a reflux pump, P-512, where it is split into two separate streams. One portion, Stream 21, is fed to the pump, P-514, and is sold as a 90 mol% pure benzene/toluene mixture. The second portion is returned to the column to provide reflux.

Stream 22, the bottoms product from T-511, contains 99.5% of the ethylbenzene fed to the column and is sent to a distillation column, T-512, at 116 °C and 55 kPa. T-512 contains 122 real sieve trays and operates with a top tray pressure 25 kPa and a bottom tray pressure of 55 kPa. The overhead vapor stream from the column, which contains 99% of the ethylbenzene fed to the column, is condensed using cooling water in E-520. The condensate is collected in a reflux drum, V-513. The stream leaving V-513 is split into two separate streams. One of the streams, Stream 23 is fed to a pump, P-516. The stream exiting P-516, Stream 29, is sent to the feed section as a recycle stream at 93°C and 210 kPa and is mixed with the ethylbenzene in Stream 1. The second stream is returned to the column, T-512, to provide reflux. Stream 24, the bottoms product from T-512, contains essentially all of the styrene that was fed to the column, and it is pumped to a pressure of 200 kPa, via pump P-515. The stream exiting the pump, Stream 27, exits the process as the 99.5 wt% pure styrene product.

Discussion:

The results stated that the five adiabatic plug flow reactors are the optimized case for the styrene process. This is quite different from the base case which uses two plug flow reactors in series. By using the Equation 6, we found that the velocity through the packed bed was unrealistically high when paired with a reasonable pressure drop (5).

$$\frac{\Delta p}{L} = \frac{150 V_o \mu}{{\Phi_s}^2 {D_p}^2} \frac{(1-\varepsilon)^2}{\varepsilon^3} + \frac{1.75 \rho V_0^2}{\Phi_s D_p} \frac{1-\varepsilon}{\varepsilon^3} \quad (6)$$

We obtained two different scenarios for reactor designs from class. In order to optimize both the isothermal reactor and the adiabatic reactor, we ran multiple case studies on certain reactor parameters to get an idea of which conditions gave the optimized case. With both sets of optimized reactors in hand, we performed an economic analysis of both systems. Our calculations show that the adiabatic reactors had the potential to produce more profit than the isothermal plug flow reactors. Most of the difference in profit came from the decreased raw material cost in the adiabatic reactor due to increased recycled ethylbenzene

After choosing the adiabatic reactors for our process, we designed a simple feed section almost identical to the base case in order to satisfy the optimized inlet conditions (temperature, pressure, and steam to ethylbenzene ratio). We later modified the feed section via heat integration. This reduced the duty required for H-511 to superheat the steam, thereby reducing utility and FCI costs. After heating Stream 4, the reactor effluent, Stream 11, heats the ethylbenzene stream, Stream 2, in E-511, removing the need for high pressure steam. Overall, the heat integration

on the process reduced the utility cost by approximately $12 million/yr compared to the base case.

Looking into the separation section, we noticed the original fuel gas compressor had a compression ratio greater than 3. In order to abide by the heuristics, we replaced it with two compressors with an intercooler. We also noticed that we lose an appreciable amount of ethylbenzene and styrene in V-511. We attempted to decrease this loss by adjusting the flash parameters. Case studies showed that reducing the temperature and increasing the pressure of Stream 15 decreased the ethylbenzene and styrene lost in Stream 16. We achieved the modified conditions by adding C-512 and increasing the duty of E-516. After looking at the flash conditions we investigated purifying the benzene/toluene stream in order to increase revenue. An economic analysis showed that we could potentially sell this stream for roughly $9 million /yr. This led to the change in specifications for T-511. We reduced the top tray pressure and temperature in T-511 to 35 kPa and 63.4 °C. These changes helped to get a better separation of the components in the tower. The increase in separation produced more benzene and toluene in the distillate stream. This allows us to sell the stream for 50% of the pure benzene and toluene prices, an option that was not viable in the base case.

Alternatives that we explored during optimization included further purifying the benzene/toluene stream, the location of C-512, and heat integration. The main alternative to the 90 mol% benzene/toluene stream is a 99.5 mol% benzene stream that we can sell at full price. To achieve this, we need to implement a third distillation column with the associated heat exchangers and vessel. Our analysis

showed that we would gain roughly $900 thousand/yr by implementing this third distillation column. The $900 thousand/yr is a much lower profit than selling the 90 mol% benzene/toluene stream for $9million/yr. Therefore, we decided to not use a third distillation column. C-512 is placed between E-515 and E-516 because this is the last and coolest point where the process stream is a vapor. This minimizes the work done by the compressor. We investigated multiple placements for C-512. When placed earlier in the process, the duty and utility cost increase for C-512. Preheating Streams 1 and Stream 29 is an alternative to preheating Stream 2 with the reactor effluent. We concluded that separating the effluent into two separate streams in order to preheat in this fashion is not as economically profitable as keeping the stream together.

Our optimized process does have design concerns. Refer to Table 11 to see these concerns and their respective justifications.

Table 11: Process Conditions Matrix

Equipment	**Reactors and Separators**		**Other Equipment**	
	High Temp.	Low Pres.	Exchangers	Valve
E-511			X	
E-512			X	
R-511	X			
T-511		X		
T-512		X		
V-511		X		
V-512		X		
V-513		X		
Valve 1				X

Table 11: Process Conditions Matrix (cont.)

Unit	Cause for Concern	Justification
E-511	ΔT_{LM}>100	Lower utility cost than having a lower ΔT_{LM}
E-512	ΔT_{LM}>100	Lower utility cost than having a lower ΔT_{LM}
R-511	High Temp.	Favorable equilibrium conversion for endothermic reaction.
T-511	Low Pressure	Styrene can't be above 125ºC so we must operate at low Temps and Pressure.
T-512	Low Pressure	Styrene can't be above 125ºC so we must operate at low Temps and Pressure.
V-511	Low Pressure	Styrene can't be above 125ºC so we must operate at low Temps and Pressure.
V-512	Low Pressure	Styrene can't be above 125ºC so we must operate at low Temps and Pressure.
V-513	Low Pressure	Styrene can't be above 125ºC so we must operate at low Temps and Pressure.
Valve 1	Large ΔP	Expander doesn't work due to the high loss of thermo energy.
Mixing Streams 31 & 32	Greatly Differing Temperatures	Steam is needed to provide a driving force for mass transfer.
T-512	Column Height	Heuristic for Column Height of 53 m max, so modify dimensions

Conclusion & Recommendations:

The base case as presented is not possible. The reactors presented in the base case will produce a choked flow due to the extremely high pressure drop. We recommend five adiabatic reactors in parallel to achieve the required production rate. The inlet stream to the reactor needs to have temperature and pressure conditions of 685 °C and 190 kPa with a steam to ethylbenzene ratio of 15.6. Furthermore, using the reactor effluent, Stream 10, to preheat the low-pressure steam in E-512 before it enters H-511 lowers the fuel gas cost by more than 50%. Employing the stream exiting E-512, Stream 11, to vaporize the ethylbenzene feed stream in E-511 also reduces utility cost. This heat integration reduces the total utility cost from the base case by $12 million/yr. The addition of C-512 and E-516 allowed us to reduce the temperature and increase the pressure of Stream 15 leading to the liquid/liquid/vapor separator. By changing these conditions, we are able to increase the styrene in the product stream and the ethylbenzene in the recycle stream. This reduces the raw material cost and takes more of the styrene produced in the reactor to actual product. Modifications to T-511 of lowering the top tray temperature and pressure gave the process the ability to sell a 90 mol% benzene/toluene mixture. The separation section optimization increased the revenue for the process by $15 million/yr. Changing the construction materials for T-511 and T-512 from titanium to carbon steel greatly reduces the FCI. The total decrease from the base case in FCI after these changes is $117 million. The new NPV of the optimized process is -$412 million. This NPV gives an EAOC of $72.9 million which is well below the projected $160 million/yr to buy styrene.

With these considerations in mind, we recommend further optimization on the process and a more detailed estimate of the NPV. Specific areas for further optimization include the flash conditions of V-511, reactor design, and calculating the pressure drops across the distillation columns. Although our optimizations saved a large amount of styrene and ethylbenzene from being lost to fuel gas in V-511, a significant amount of ethylbenzene is still being lost. We recommend looking into V-511 for a better optimization. Further optimization of the reactor to increase the yield of ethylbenzene to styrene is also a strong recommendation.

Safety and Environmental Concerns:

The first and foremost goal of an optimization project is to design a process that is safe for others, yourself, and the environment. Our optimized styrene process presents plant operators with a few potentially hazardous situations. High temperatures and pressures exist in many areas of the process especially in the heat exchangers, reactors, and piping. In order to safely operate these pieces of equipment, correct placement of appropriate insulation is a necessity. Vessels and pipes with high-pressure fluids must employ safety valves where needed. Careful and regular maintenance of the process control systems is a requirement for any safe process operation. Also, thorough training of operators in the system controls and emergency protocols is very important to the health and safety of the plant and the people in it. Operators, maintenance crews, and contract labor need to wear the appropriate personal protective equipment at all times when inside the plant. Following the guidelines presented by OSHA, the Occupational Safety and Health Administration, is a good safety practice.

A few environmental concerns are also present in our process. The wastewater exiting the plant contains traces of organics. Before wastewater enters the environment, treatment and removal of the organics needs to take place. The fuel gas stream that is being sold also contains some noncondensable gases that could be harmful to humans or the environment when burned. Proper containment of these gases and the fuel gas burned in the fired heater is a significant environmental safety concern for this process. Careful observing EPA regulations for wastewater and fuel gas is essential to preserving the environment. Safety

considerations need continued re-evaluation as further design optimizations take place

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Appendix:

Table of Contents

Local Heat Transfer Coefficients

Heat Transfer To	h (W/m^2K)
Liquid Organic	600
Condensing Steam	6,000
Boiling Organic	5,000
Vapor Organic	100
Desuperheating Steam	200
Boiling Water	8,000
Cooling Water	1,000
Partially Condensing Organic	3,000
Condensing Organic	1,500